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June 1978

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Structure Sensitivity in the Electrocatalytic Properties of Pt:
I. Hydrogen Adsorption on Low Index Single Crystals and the Role of Steps

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ABSTRACT

Single crystal surfaces were used to examine the structure sensitivity of hydrogen chemisorption on Pt in dilute acid electrolyte. An electrochemical cell was coupled directly with an ultra-high vacuum system and low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) were used to determine the structure and composition of the electrode surfaces. Hydrogen adsorption was examined by triangular sweep cyclic voltammetry. Contributions to the multiple peaks observed in voltammograms of Pt due specifically to anions were deduced and the effects of surface geometry alone were determined. A difference in hydrogen bond energy (3.4 kcal/mole) was observed for hydrogen on the (111)-(1x1) and the (100)-(1x1) surface. Hydrogen was also found to be more strongly bound at (~ 4 kcal/mole) at (100) steps than on the atomically flat (100) surface. Hydrogen adsorption on highly ordered surfaces could be described quantitatively by the classical model for single site adsorption on a homogeneous surface with a weak interaction between nearest neighbor pairs. This repulsive interaction lowers the coverage at OV (NHE) of hydrogen on a perfect (111) surface to less than a monolayer. Some evidence is presented suggesting that anion adsorption is also structure sensitive, and that the "third" anodic peak observed on Pt polycrystals in 1N H₂SO₄ is due to structure sensitive anion adsorption.

Structure Sensitivity in The Electrocatalytic Properties of Pt:I
Hydrogen Adsorption on Low Index Single Crystals and the Role of Steps

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Introduction

Single crystal surfaces of controlled and known structure can be used to isolate the effect of site geometry on the electrocatalytic properties of electrode surfaces. Of particular practical importance is the determination of site specificity in the electrocatalytic properties of small (~ 1 nm) clusters of metal atoms, such as one has in the case of highly dispersed Pt on carbon [1]. The geometry of the surface atoms in these clusters depends on the packing geometry, the number of atoms in the cluster, and the shape of the cluster, e.g. octahedrons, cubo-octahedrons, icosahedrons, etc. Various thermodynamic calculations have been proposed [2-4] to predict the equilibrium cluster geometry as a function of the number of atoms per cluster, but there is at this time no experimental confirmation of any of these models. It is possible, however, to simulate nearly all of the different surface coordinations which may occur on clusters by the use of single crystals, and to learn a priori whether cluster geometry has an important effect on catalytic properties.

In this work, single crystals are used to isolate structure sensitivity in the electrocatalytic properties of Pt surfaces in aqueous acid electrolyte. In part I, the sensitivity of the Pt-H_{ads} bond energy to the surface structure is studied using the low index surfaces of (111) and (100) orientation and a stepped surface with a high periodicity of monatomic steps prepared from a single crystal of (211) orientation. These same surfaces are used in part II in the study of the structure sensitivity of the oxygen reduction reaction. The interpretation of multiple peaks for H adsorption-desorption in the cyclic voltammogram of polycrystalline Pt in acid is still controversial in spite of many years of investigation. A central issue in the interpretation is the association of distinct peaks with

surface sites of different atomic coordination, often referred to as intrinsic heterogeneity. The method of isolating this contribution is to use single crystal surfaces of well defined structure containing sites of only certain coordination numbers. Previous studies [5,6] using cyclic voltammetry on single crystals showed only that the relative heights of the different peaks varied between the low index faces (111) and (100). The true surface geometries on the crystals used were unknown, and the surfaces were pretreated by repeated triangular wave potential cycling between 0-1.5V (RHE) to obtain a "clean" surface. Reflection electron diffraction has shown [7] that the latter changes the structure of the Pt surface to a depth of several hundred nm. In the present investigation, a definitive characterization of the surface structure of Pt single crystal electrodes was obtained using low energy electron diffraction (LEED). Atomically clean electrode surfaces were obtained in ultra-high vacuum by ion-bombardment/anneal cycles, and electrode surface composition was monitored using Auger electron spectroscopy (AES). Preliminary results from this work have been published [8] and the present report is a more complete description of all experiments conducted during this study. After submission of this report for publication, results from similar kinds of experiments with Pt single crystals were published by Hubbard et. al. [33]. A discussion comparing the results and conclusions from these two independent studies is given at the conclusion of the text.

The interpretation of cyclic voltammograms of Pt in acid is complicated by the effects of anion adsorption on the hydrogen bond energy. Anion adsorption from dilute H_2SO_4 has been shown [8,9] to cause major shifts in both the position and height of the H adsorption/desorption peaks which cannot be eliminated even by dilution to 10^{-5}M [9]. These studies have indicated that dilute HF appeared to be the aqueous acid electrolyte that produced the least effect on the hydrogen bond energy. In the present study, well defined Pt surfaces were studied in 1N HF and 0.1N HClO_4 in an attempt to differentiate the effects of surface structure from the effects of anion adsorption. The voltammograms in 0.1N HClO_4 were very similar to those obtained in HF, and most of the results reported here were obtained in 0.1N HClO_4 .

Experimental

A schematic diagram of the directly coupled electrochemical-LEED/AES system is given in Fig. 1a. The electrochemical cell is located inside a continuously purged glove box which is connected to a sample transfer chamber via a sealed port. The sample transfer chamber has a separate sorption-ion pumping system that can

evacuate the chamber to 2×10^{-8} torr in a few hours. Sample surfaces to be examined are mounted on a 316 s.s. block which has a threaded hole in the top. The block is held on the end of a rod attached to a rotary/feedthrough on a 14" linear motion bellows assembly via a screw-thread and can be transferred into the offset holder on the manipulator in the ultra-high vacuum bell jar. The block is detached from the transfer rod by unthreading. In the reverse procedure, the sample block is lifted into the transfer chamber, the valve closed, the chamber back-filled to ~ 1 atm with research grade argon, the transfer port opened from within the glove box, and the block brought manually into the glove box. Inside the glove box the sample, e.g. a Pt foil or single crystal, is removed from the block, mounted in a solid PTFE holder (Fig. 1b) and placed in the electrochemical cell (designated EC in Fig. 1a). The electron optics for LEED observations was a standard Varian 3-grid system. The Auger electron spectra were obtained using a Varian cylindrical mirror analyzer system with a 3 kV integral electron gun. Electron energies were analyzed in the derivative mode using standard ac modulation techniques [10]. The sample surfaces were cleaned by bombardment with 500 eV Ar^+ ions from a Varian ion gun. The ion beam could be rastered at 20 kHz over the entire surface of the sample. The samples were heated indirectly from a tungsten filament located directly at the back of the sample block. Surface temperatures were measured using an optical pyrometer.

The function of the PTFE holder was to mask off all but the center region of the crystal so that the edges of the single crystals were not exposed to the electrolyte. The area exposed to the electrolyte varied depending on the size of the single crystal, but was generally a region ca. 0.5 cm in diameter. The geometric area of the working electrode was assumed to be equal to the size of the hole in the PTFE gasket.

Aqueous 0.1N HClO_4 solution was prepared from the concentrated acid (Baker reagent grade) using triply distilled water, the final distillation passing water vapor and air through Pt/Rh gauze at 900°C . The concentrated acid was pretreated by refluxing with H_2O_2 (30%). The dilute solution was purified in the electrochemical cell by cyclic cathodic and anodic electrolysis for 24 hours. The electrochemical

cell was a small (25 ml) two chambered cell constructed from solid PTFE, one chamber containing the reference electrode (Pt black with bubbling H_2), the other the working and counter electrode (1 cm^2 Pt foil), the two chambers connected by a Luggin capillary. All gas and electrical connections were made via gas-tight feedthroughs in the glove box walls. A fast-rise Wenking potentiostat driven by a programmable function generator was employed. Voltammetric scans were recorded on an x-y recorder for sweep rates less than 0.2 v/s and on a storage oscilloscope for all faster sweep rates. All electrode potentials are referred to that of the hydrogen electrode in the same electrolyte (RHE).

The Pt single crystals were ca. 2 mm slices from single crystal rods supplied by MRC (Marz grade) of nominal orientation (111), (100) and (211). The rods were mounted on a crystal goniometer, aligned to within 2° of the desired crystallographic direction by von Laue x-ray back reflection, and spark cut perpendicular to the surface normal. The spark cut surfaces were mechanically and electrochemically polished to a strain-free mirror finish. Scanning electron microscopy indicated there were few major imperfections, e.g. scratches, etches, pits. A high purity Pt foil, ca. 1 cm^2 , was degreased by treating with fuming concentrated HNO_3 and annealed by soaking for 24 hours in H_2 at 800°C . This foil was used as a polycrystalline standard surface and was subsequently given precisely the same characterization sequence as was used for the single crystal surfaces.

A probe electrode was used periodically to monitor the cleanliness of the electrolyte. It was a 0.1 mm dia. Pt wire sheathed in PTFE to expose only ca. 0.1 cm^2 of surface. It had been subjected to more than 10^3 triangular cycles of 0-1.5V prior to use in these experiments. The characteristic voltammogram for this electrode in the 0.1N HClO_4 used is shown in Fig. 3.

Results

(a) Characterization of the pre-test electrode surfaces by LEED and AES

The surfaces were cleaned in the ultra-high vacuum system by sequential argon ion bombarding and subsequent annealing at 600°C . Repetitive bombarding and annealing continued until the Auger electron spectra indicated no signals other than those

for Pt [11-13]. The major impurities were C, P, and S, apparently migrating to the surface from the bulk 1-11 ppm during high temperature annealing. The clean, annealed (111) surface exhibited a LEED pattern with sharp, well contrasted, diffraction spots in a (1x1) array, i.e. the arrangement of surface atoms is identical to that in the bulk fcc unit cell. The degree of perfection of the periodicity (and its alteration by subsequent exposure to electrolyte) was checked qualitatively by measuring the angular width of the diffraction spots by photographic methods [14]. The mean diameter d of a periodic region is related to the angular width $\delta\theta$ of a diffraction spot by the relation

$$\delta\theta = \lambda / (2d \cos \theta)$$

where $\lambda = (150/V)^{1/2}$ is the electron wavelength (in Å), V the electron energy (in eV) and θ is the diffraction angle. The angular width of the (01) spot from the annealed surface was determined to be less than 1° , probably less than could be determined with this technique. We estimate perfectly periodic regions of at least 50Å were obtained, which puts an upper limit on the number of imperfections at 5 a/o for the clean, annealed surface.

The clean, annealed (100) surface exhibited a complicated LEED pattern with $n/5$ order spots indicative of a reconstructed surface. The Pt(100)-(5x20) surface has been the subject of numerous previous investigations [15-17] and will not be discussed here at any length. The reconstructed surface is known to be unstable in the presence of certain adsorbates, such as CO, C₂H₂, C₂H₄, and undergoes reordering to the (100)-(1x1) structure. The crystal was taken through three different stages of transfer to determine if the surface structure changed as a result of contact with electrolyte. The first stage was simply transfer into the transfer chamber, backfilling to 1 atm with argon (Airco, Research Grade), followed by the pumpdown and transfer back into the UHV chamber. The LEED pattern was unaffected by this treatment, and the Auger electron spectrum indicated only a very small carbon signal on a spectrum for clean Pt (Fig. 2b). The second stage was transfer of the crystal into the glove box and back. A LEED pattern was still visible but the $n/5$ order spots were gone and n -th order spots were diffuse with halos around the diffraction

spots, indicative of a disordered overlayer. The Auger electron spectrum showed significant carbon and oxygen KLL signals, corresponding to approximately a monolayer of chemisorbed carbonaceous molecules. The surface becomes contaminated as a result of exposure to the glove box atmosphere, and the structure of the surface is reordered to (100)-(1x1). The final stage was transfer of the crystal into oxygen-free electrolyte (no potential control), washing thoroughly with distilled water and transfer back into the UHV chamber. Exposure of the crystal to either electrolyte or distilled water resulted in complete loss of the LEED pattern. The Auger electron spectrum was primarily carbon and oxygen, with the Pt signals reduced by almost an order of magnitude from the signals for the clean surface (Fig. 2d). It has been reported by other investigators and confirmed in the present work that low Z (< 40) overlayer atoms can be removed from a high Z metal substrate by low energy (< 500 eV) argon (or oxygen [17]) ion bombardment without disturbing the substrate surface structure. A 5×10^{-3} Coul/cm² bombardment of argon ions at 500 eV completely removed the contamination (Fig. 2e) and produced a reasonably sharp (1x1) LEED pattern for the crystal exposed to oxygen-free electrolyte.

The (211) surface can be described in terms of the classification of stepped surfaces suggested by Lang et. al. [18]. The ideal (1x1) structure for this surface is shown in Fig. 4 and in the notation of Lang et. al. the structure is Pt(S) [3(111)-(100)]. This surface is similar to the Pt(S) [6(111)-(100)] (nominal Miller index 775) studied by Somorjai and co-workers [19] except that it has twice the number of steps per unit area. The expected LEED pattern for this structure is shown in Fig. 6 (the calculation of the diffraction pattern is given in the Appendix) along with the observed pattern at 145V. The splitting of the (01) spots is inversely proportional to the terrace length and is exactly the expected amount. The step height was calculated from the intensity of the split spot as a function of energy [18] and was found to indicate the monatomic step height expected. This surface was stable with respect to transfer to the electrochemical cell and exposure to oxygen-free electrolyte, i.e., no reconstruction occurred.

The polycrystalline foil surface was cleaned in the UHV system using the same ion-bombarding-annealing sequence used for the single crystals until no trace of

surface contamination could be detected by AES. Examination of the clean, annealed surface by LEED did not reveal any preferred orientation.

(b) Electrochemical characterization of electrode surfaces.

It was concluded that the single crystal surfaces upon transfer from the UHV system into the oxygen-free electrolyte (an equivalent open circuit potential of 0.5-0.6V) were well-ordered (1x1) structures of a high degree of perfection, but with at least a monolayer of adsorbed impurities. It was recognized before any electrochemistry had been done with these surfaces that the "as transferred" surface was not clean, and the electrochemical characterization might also require some in situ electrochemical method of stripping the adsorbates without altering the surface structure. The approach followed here was to use the "as transferred" annealed polycrystalline foil to establish the minimum electrochemical treatment required to produce a voltammogram which would be generally accepted as indicative of clean Pt. The literature abounds with voltammograms which are purported to be characteristic of the "clean" surface of polycrystalline Pt and no effort will be made here to review it. The study by Conway et. al. [6] was used for the reference voltammogram in 0.1N HClO₄, and the Pt probe electrode produced a voltammogram in our electrolyte that is essentially identical to that in Ref. 6. There is the possibility that the Pt electrodes used in previous studies, which were usually extensively cycled between oxide formation and reduction, do not represent the properties of the clean, annealed Pt surface, but in fact were distorted, non-equilibrium surfaces, possibly containing oxygen in some form. This possibility could be easily checked in the present work. The same electrochemical treatment applied to the polycrystalline foil electrode was applied to the single crystal electrodes, and the resulting structure and composition of the electrode surface was determined by post-test analysis using LEED and AES. This analysis is discussed in detail below. In brief, an in situ electrochemical pretreatment was found which removed the contamination and did not severely alter the Pt surface periodicity or subsurface structure.

Figure 6 shows the initial voltammogram for the polycrystalline foil electrode after transfer from the LEED/AES system. The initial voltammogram has two features

characteristic of all the surfaces examined: a skew similar to that produced when the Ohmic resistance is large but with the opposite dependence on sweep rate, i.e., increasing sweep rate decreases the skew; no oxide formation at potentials below 1.0V. Since AES showed that a clean surface is contaminated by adsorption of a carbonaceous species before it is placed in the cell, the skew and lack of oxide formation were taken to be indicative of a poisoned surface. The pretreatment used to remove this contamination was a series of 1s anodic pulses to 1.5V, the pulse rise time being less than 1 ms, with a 10s hold at 0.5V to reduce the oxide. The condition of the surface was monitored using the voltammogram recorded between 0-0.9V. The electrode surface was considered to be clean when the pretreatment cycle produced no change in the voltammogram. For most of the experiments, as shown in Fig. 6, 10 cycles was sufficient and in some cases only one or two were necessary. The voltammogram for the clean, annealed, polycrystalline Pt surface has a high degree of structure in the hydrogen adsorption-desorption region with three peaks clearly discernable on the anodic sweep and reasonable correspondence between the anodic and cathodic peak potentials (allowing for Ohmic resistance in dilute electrolyte). The ultra-high vacuum annealed surface shows a high binding energy peak (labelled V) not seen (with the probe electrode) on a Pt surface that has been subjected to extensive Pt oxidation-reduction cycling. The ratio of the total measured charge to the charge calculated for the measured geometric area of the foil assuming $210 \mu\text{C}/\text{cm}^2$ was 0.85.

The single crystal electrodes were placed in the electrochemical cell and given exactly the same pretreatment as given the polycrystalline foil. During the course of this study, at least two different crystals of each orientation were used, and the entire experiment repeated with each at least five times. The resulting voltammograms were not reproducible in detail, but certain major features were seen consistently. The voltammograms and isotherms shown in Figs 7 to 9 are each from a single observation but represent the major features seen in all the experiments. The number of hydrogen atoms adsorbed (in coulombs) at any potential is q

$$q = A^{-1} \int i_H dt = A^{-1} \int (i - i_{dl}) \frac{dE}{v}$$

where v is the sweep rate, i_{dl} the double layer charging current, A the geometric area of the electrode. For subsequent use Q is defined as the saturation quantity of hydrogen adsorbed at equilibrium (0V or 1 atm. H_2). The isotherms for the (111) and (100) surfaces clearly indicate that hydrogen is more strongly bound on the (100) surface, and that the two major peaks (I and IV) in the voltammogram of polycrystalline Pt can be related to H_{ads} at sites of (111) and (100) nearest neighbor coordination, respectively. The voltammogram for the stepped surface [3(111)-(100)] (Fig. 9) indicates quite clearly the effect of steps on the hydrogen bond energy. A comparison of the voltammograms for the atomically flat (111) surface and the stepped (111) surface, as done in Fig. 9a, shows that ≈ 50 a/o of the charge on the stepped surface is associated with hydrogen adsorbed at potentials anodic of 0.2V. Since approximately 30 a/o of the geometric area of the [3(111)-(100)] surface is associated with steps, it seems reasonable to associate the hydrogen which is adsorbed at 0.2-0.4V with the (100) steps. Of the hydrogen bonded at the (100) steps, about 10 a/o is adsorbed at potentials above 0.35V, i.e., more strongly bound than on the atomically flat (100) surface.

The saturation charge for adsorbed hydrogen was not a very reproducible quantity, particularly for the (111) surface. That is while the shapes of the voltammogram and the location of peaks were reasonably reproducible, the amount of charge under these curves was variable. There could be considerable error in the assumed geometric area of the electrodes contacted by electrolyte, but this is not likely to be different from one electrode to the other and probably represents an uncertainty of $\approx 10\%$. The variations observed were felt to arise from uncontrolled levels of surface contamination or electrolyte impurities. The coverages given in Figs. 7 to 9 were among the highest observed. The ratio of Q/Q_{geo} , where Q_{geo} is the charge expected assuming one H atom per surface Pt atom, should be a measure of the H/Pt stoichiometry for a given surface. The surface atom densities used to compute Q/Q_{geo} were 1.62×10^{15} for the (111) surface, and 1.30×10^{15} for the (100) surface. The (111) density was used for the stepped surface since it is unlikely that the H/Pt stoichiometry would be the same at a step as at the terrace ($H/Pt < 1$).

The values of Q/Q_{geo} for all the surfaces investigated were ≈ 0.9 , in reasonable agreement with the expectation of $H/Pt \approx 1$, except the (111) surface for which a significantly lower value was observed consistently. This is felt to be a real difference in H/Pt stoichiometry for the (111) surface relative to the (100) surface.

(c) Characterization of the post-test structure by LEED and AES

After electrochemical characterization of an electrode surface, the electrode was removed from solution while potentiostated at 0.5V, rinsed several times with the distilled water, mounted on the holder block and transferred to the LEED/AES system. All sample handling was done in the glove box. As discussed previously, the surface composition analysis by AES of surfaces transferred from solution always showed at least monolayer amounts of carbonaceous contamination, as characterized by the spectrum in Fig. 2d. Careful low energy argon ion bombardment was used to remove this contamination layer and examine the surface structure by LEED. The amount of ion bombardment necessary to produce the sharpest observable LEED pattern on a (111) surface that had been placed in electrolyte but never cycled was measured repeatedly, and was used to establish a standard criterion. This criterion was the ratio of the peak to peak height of the C_{270} transition to the Pt_{236} transition; the LEED pattern was analyzed when this ratio was $0.2 \pm .02$. The diffraction spots were always less intense and of greater angular half width after the electrolyte-ion bombardment cycle. The reproducibility of post-test LEED patterns was only fair with regard to a quantitative measurement of the angular width of diffraction spots. All of the single crystal surfaces potentiostated at 0.5V for a prolonged period produced (1x1) LEED patterns with (01) spots of angular width $3 \pm 1^\circ$. The pretreatment cycle shown in Fig. 6 used to clean the surfaces in the electrochemical cell had no effect on the LEED pattern. It was concluded, therefore, that the single crystal voltammograms shown in Figs. 7 to 9 are representative of their respective (1x1) surface structures with perfectly periodic regions on the order of 20-30 $\text{\AA}$. The periodicity of the surface structure determined by the methods used here can be viewed as a lower bound on the periodicity, since some ion bombardment

was used which could have damaged the Pt surface while removing the carbonaceous adsorbate. It seems reasonable to conclude that the size of (1x1) regions of the "as-tested" single crystal surfaces was at least $20\text{\AA}$ and/or the number of imperfections was less than 15 a/o.

Some experiments were conducted to determine the effect of slow triangular wave potential cycling through the oxide formation region on the LEED pattern. The sweep rate used was 100 mV/s, and the number of cycles fixed at 10. The only variable was the anodic limit, which varied from 0.6V to 1.5V. Figure 10 shows the relationship observed between the angular width of the (01) spot in the resulting LEED pattern and the anodic potential limit. No LEED pattern could be observed when the potential exceeded 1.2V, indicating total disruption of the surface periodicity. Cycling to a potential limit in the region 0.9-1.2V produced diffuse, poorly contrasted, poorly reproduced diffraction patterns indicating a random disordering of surface atoms with regions of periodicity reduced to only $5\text{-}10\text{\AA}$. The loss of the (1x1) surface periodicity was correlated with systematic changes in the voltammograms of the (111) and (100) surfaces, as shown in Fig. 11. When these electrodes were subjected to oxidation-reduction cycles that disordered the surface as seen by LEED, new peaks appeared in the voltammogram of each crystal characteristic of the other face, i.e., the (111) surface developed a peak at $\approx 0.3\text{V}$ and the (100) surface developed a peak at $\approx 0.1\text{V}$, and the (100) surface develops a hydrogen peak seen only on the $[3(111)-(100)]$ stepped surface which was associated with hydrogen bonded at (100) steps.

The Auger electron spectra of the post-test surfaces did not show any measurable quantity of oxygen on or in the Pt surface as a result of the standard electrode pre-treatment. Rinsing electrolyte from the electrode surfaces with water appeared to remove all HClO_4 , as only a very small Cl peak was seen, and apparently complete sublimation of H_2O from the surface was accomplished when the electrodes were placed in ultra high vacuum. A small O_{512} peak was seen on every Pt surface exposed to the glove box atmosphere which was probably associated with adsorbates like CO. No oxygen was detected that could be associated with the Pt surface or subsurface lattice. This was true even with the surfaces cycled to 1.5V.

Discussion

Before a discussion on the interpretation of the voltammograms and isotherms observed is presented, it is of interest to consider how the raw data differs from that in previous investigations. The voltammograms for Pt (111), (100) and (110) reported by Will [5] and Angerstein-Kozłowska et. al. [6] were for surfaces which have been subjected to slow oxide formation-reduction potential cycling that, as shown by the LEED observations in this work, produced a disordering of the surface. The loss of surface periodicity was clearly correlated with the appearance of "new" peaks, indicating the new peaks originated from sites on the disordered surface. The voltammograms in these previous investigations indicated all four peaks (designated I-IV) are seen on each of the single crystals used (only on the (100) was peak V seen) but with varying amounts of charge associated with each. Qualitatively both showed $Q_I > Q_{IV}$ on (111) and $Q_{IV} > Q_I$ on (100). In the recent work of Bronoel et. al. [20], slightly different results were observed with surfaces cycled in 1N H_2SO_4 10^2 times at 100 mV/sec and 0-1.3V. Using scanning electron microscopy (SEM), they found that single crystals prepared by conventional cutting and polishing suffered extensive surface damage during potential cycling. Instead they prepared ordered faces by chemically induced faceting of single crystal spheres. Potential cycling did not produce damage to these surfaces that could be observed by SEM (resolution on the order of $10^3 \text{ \AA}$). The voltammogram for the (111) face was essentially the same as that found here if the effect of $SO_4^{=}$ anion is taken into account, i.e., $SO_4^{=}$ anion adsorption causes a splitting of the single peak at $\approx 0.1V$ [9]. The voltammogram for the (100) face in 1N H_2SO_4 was similar to that reported by Will, i.e., both peaks I and IV. Although surfaces may appear smooth in SEM, they are not necessarily smooth on the atomic scale, and as shown by LEED are not ordered on the atomic scale when potential cycled in the manner employed in these previous investigations.

The hydrogen adsorption isotherms observed for the (1x1) single crystal structures used in this work show clearly that the bonding of hydrogen to Pt is sensitive to the nearest neighbor coordination of the adsorption site. Following

the established convention, we define the standard adsorption free energy as the electrochemical potential at which the coverage ($\theta/\theta_{\text{max}}$) is 0.5. The adsorption free energies for hydrogen on the highly ordered surfaces are shown in Table 1 with the equivalent peak(s) in the voltammogram of a polycrystalline Pt surface designated. The minor peaks designated II and III observed with the probe electrode were not clearly evident on any of the (1x1) surface structures or on the well-annealed polycrystals. One of the peaks, designated V, was observed only with the stepped surface and is clearly associated with sites found only at steps. The easiest way to see this is to attempt to construct the voltammogram for the stepped surface from the sum of the (111) and (100) voltammograms scaled by a factor that reproduces the heights of peaks I and IV, as done in Fig. 9. There are adsorption site geometries present at monatomic steps which are not present on the (1x1) surfaces of (111) or (100) orientation. These are the five-fold coordination sites, denoted B_5 in Fig. 12, and the two-fold sites (B_2) that are formed along the outer edge of the step. There is no fundamental theory of adsorption presently available which can be invoked to predict an association between adsorptive bond energy and site geometry, i.e., we cannot associate peak V with the B_5 sites or the B_2 sites directly. One can conclude from the voltammetry of oriented stepped surfaces presented here that some sites associated with steps exhibit a somewhat higher (~ 3 kcal/equiv) binding energy than the flat surface of identical orientation and become occupied first.

Detailed studies of the Pt-H_{ads} bond on highly ordered surfaces in the absence of electrolyte (vacuum interface) using LEED, AES, electron energy loss spectroscopy, work function measurement, and flash and thermal desorption spectroscopy (TDS) have recently appeared. The TDS studies of Schmidt and co-workers [21] and Lu and Rye [22] on the (111) and (100) surfaces are in qualitative agreement with differences in Pt-H_{ads} bond energy found here in that they find hydrogen to be more strongly bound on (100) than the (111) surface. Lu and Rye concluded that the desorption spectrum for the (211) surface was a composite of desorption from the individual (111) and (100) regions weighted by the 2:1 geometric ratio. The more refined work

Table 1

Characteristic Hydrogen Peaks and Adsorption Free Energies on Pt

<u>Surface Structure</u>	<u>Saturation Coverage[*]</u>	<u>Δg^0 (kcal/equiv)</u>	<u>Equivalent peak for polycrystalline Pt</u>
(111)-(1x1)	≈ 0.7	- 1.15	I
(100)-(1x1)	0.88	- 5.30	IV
(S)[3(111)-(100)]	0.35 terraces	≈ -1	I
	0.45 steps	≈ -5	IV
		- 9.2	V

*the coverage obtained by extrapolation of the isotherm to OV (NHE).

of Christmann and Ertl [23], which supplemented TDS with work function measurements, concluded that hydrogen bonded at monatomic steps have slightly higher (2.5 kcal/atom) binding energies than on the equivalent flat surface, and that there are two distinct states for H_{ads} at steps having slightly different dipole moments, both of opposite sign to that for H_{ads} at the flat surface. Again there appears to be at least qualitative agreement in the Pt- H_{ads} bond energy at steps between the gas-phase and electrochemical observations.

One might expect that adsorption on a perfectly periodic single crystal surface with a homogeneous site geometry (e.g. fcc (100) and (111)) in the absence of interaction between adsorbed species the adsorption isotherm would be Langmuirian,

$$\frac{1-\theta}{\theta} = (a_{H^+})^{-1} \exp(+\Delta g^0/RT) \exp(EF/RT)$$

where Δg^0 is the standard state ($\theta=0.5$) adsorption free energy. A Langmuir isotherm applied to hydrogen adsorption on the (100) does not fit well as Fig. 8 indicates. Lateral interactions between adsorbed hydrogen atoms must be accounted for quantitatively to produce a theoretical isotherm in agreement with the observed. The effect of a repulsive (or attractive) interaction between nearest neighbors on a lattice of uniform localized sites was worked out for both mobile and immobile films by Wang [24] and the results summarized and elaborated upon by Roberts [25]. If V is the interaction energy between nearest neighbors, and the Boltzmann factor $\eta = \exp(-V/RT)$, then for a mobile film the heat of adsorption ($w = -\Delta h$) will decrease with coverage as

$$w(\theta) - w(\theta=0) = -\frac{1}{2} zV \left[1 - \frac{1-2\theta}{\{1-4(1-\eta)\theta(1-\theta)\}^{\frac{1}{2}}} \right]$$

where z is the number of nearest neighbors at a site. When the interaction is very weak or the temperature very high $\eta \approx 1$, and

$$w(\theta) \approx w(\theta=0) - zV\theta$$

an approximately linear variation results. In the case of immobile adsorption, the change in Δh is nearly linear but saturation coverage occurs at about $\theta = 0.9$ [25]. In the case of weak nearest neighbor interaction, therefore, the isotherm is

$$\left(\frac{1-\theta}{\theta}\right) = (a_{H^+})^{-1} \exp(+\Delta g_1^0/RT) \exp(EF/RT) \exp(+r\theta)$$

where $r = zV/RT$ and Δg_1^0 is now the initial (zero coverage) adsorption free energy. Equations of this form have been used previously by Conway and co-workers [26], but no physical significance was given to the parameter r as we have done here. For adsorption on the (100) surface, the excellent fit shown in Fig. 13 to the observed isotherm was obtained using $V=4.2 \times 10^{-14}$ ergs /H pair, $z = 4$ and $\Delta g_1^0 = -6.44$ kcal/equiv. The same value of V was used for the (111) surface, with $z = 6$ and only Δg_1^0 was adjusted and θ was defined as q/Q_{geo} , the measured charge to the theoretical maximum charge for one adsorption site for Pt surface atom. The theoretical isotherm for $\Delta g_1^0 = 3.0$ kcal/equiv agrees well with experiment and illustrates in a physically meaningful way why q/Q_{geo} for the (111) surface is significantly less than unity at potentials anodic of 0 V (NHE). On the close packed (111) surface, the repulsive interaction between adsorbed H atoms is large enough relative to the adsorption energy on this surface to cause only every other site to be occupied, i.e., the progressive filling of an ordered (2x2) structure. On the less closely packed (100) surface the adsorption energy is high enough relative to the repulsive interaction that all possible sites are filled to saturation. A similar effect would occur with H adsorption on the (111) terraces of stepped surfaces but there are complications to the analysis in this case. Here, of the 3 atoms that form the terrace, only one has exactly the (111) nearest neighbor configuration, the other two atoms have some association with the step. Therefore, although the geometric area ratio of terrace to step is 2:1, we cannot expect the charge ratio to be 2:1, nor would the repulsive interaction model necessarily apply directly to the [3(111)-(100)] surface. With stepped surfaces of longer (111) terrace or with well-annealed polycrystalline surfaces, the model derived here for the (111) surface would be applicable. Thus, well annealed polycrystalline surfaces consisting of microstructures of principally (111) and (100) orientation would be expected to produce a voltammogram which is a composite of the individual voltammograms of the adsorbed (111) and (100) surfaces. Qualitatively, the voltammogram of the well-annealed polycrystal (Fig. 6) can be constructed as a composite of the individual

voltammograms, attributing peak V to absorption at residual point defects (step-like geometry).

The fine structure, notably peaks II and III, observed in voltammograms of Pt electrodes subjected to extensive potential cycling (as in Fig. 3) were not clearly in evidence for any of the surfaces studied using the electrochemical-LEED/AES system and procedures. There appeared to be unresolved structure in the voltammograms of the well-ordered surfaces which might be related to peaks II and III. For the (111) surface, this is evident as a shoulder at $\approx .2V$ in Fig. 7a and for the (100) this is observed as the departure from the theoretical (broadened) isotherm at $\approx .2V$ in Fig. 13. Previous studies of the fine structure indicate that it is resolved only with clean surfaces and clean electrolyte, the clean surfaces being produced by potential cycling. That the electrolyte was clean is evidenced by the voltammogram using the probe electrode (Fig. 3). It may be that the lack of resolution is due to some residual contamination of these surfaces which is not removed by the pretreatment sequence. However, an observation reported previously [8] by this investigator showed that the addition of $SO_4^{=}$ anion to dilute HF resolves and enhances the unresolved fine structure on the (111) voltammogram in HF (or $HClO_4$). This observation leads to the unavoidable consideration of the relation of peaks II and III to anion effects, to the coupling of anion desorption and hydrogen adsorption, and to structure sensitive anion effects.

• The use of highly ordered Pt electrode surfaces has shown that differences in adsorption site geometry are associated with the changes in adsorption free energy as large as 6 kcal/equiv. It has been shown [8,9] that specific adsorption of anions such as $SO_4^{=}$, HSO_4^{-} , and $H_2PO_4^{-}$ couples with the hydrogen adsorption process to produce changes in Pt- H_{ads} bond energy on the order of 0.5 kcal/equiv. Anion effects (other than Cl^{-} or I^{-}) are, therefore, second order effects relative to the role played by site geometry. We might anticipate that anion adsorption is also structure sensitive, and in fact Schuldiner and Rosen [27] found that the specific adsorption of $SO_4^{=}$ on Pt was greater on rough surfaces than on smooth surfaces. As shown previously, specific adsorption of $SO_4^{=}$ on the (111) surface gave rise to a distinct peak at about the potential of zero charge [27,28] and to a shoulder on the main peak (the

voltammogram is reproduced in Fig. 14). The faradaic reaction taking place is probably a coupled process as suggested by Huang et. al. [9]

The anodic peak potential for this reaction was observed to be exactly the same potential as the peak designated III in the voltammogram for polycrystalline Pt. These results suggest that peak III in these voltammograms is due to specific adsorption of anions at the pzc.

In their study of the stepped Pt surface, Christmann and Ertl postulated that there is a net positive charge at edge atoms at the vacuum interface. Some model computational studies on the local densities of state at steps and on orbitals associated with steps have been carried out. Bonding orbitals were formed at edge atoms which were not present on the flat surface [29] and surface states were observed 3 eV below the Fermi level in the local density of states at edges [30]. It is unlikely that properties like the surface dipole moment or the local density of states at the Pt-vacuum interface would apply directly to the Pt-aqueous acid interface. In the absence of equivalent quantum mechanical calculations for the Pt-electrolyte interface, we may only speculate that qualitative characteristics of the Pt-vacuum interface may apply to the Pt-electrolyte interface, as seems to be the case for the relative effects of site geometry on Pt-H_{ads} bond energy at the different interfaces. It may be that at the potential of zero charge (pzc) atoms of low coordination carry a net positive charge and that there is, therefore, adsorption of anions at such sites at the pzc even for anions that are not specifically adsorbed on the flat surface. It is suggested that in electrolytes which are non-adsorbing on atomically flat surfaces, specific adsorption may occur at imperfections or discontinuities in the surface, accounting for the small charge for III seen with the single crystal surfaces. With potential cycled surfaces, a greater number of imperfections and adatoms are present giving rise to defined peaks near the pzc. In adsorbing electrolytes like H₂SO₄, specific adsorption occurs even on atomically flat surfaces and may occur preferentially at low coordination sites. One

might expect, according to this argument, that when the Pt is in the form of very small clusters, the number of low coordination number atoms on the surface increases significantly and the charge under peak III should increase proportionally. Just such a relation has been observed by Kinoshita et. al. [31] in voltammograms of high surface area Pt in 1M H_2SO_4 . They also observed that peak III had different (slower) kinetic behavior than the other peaks as seen from the dependence of the peak potential on the sweep rate. It would not be unexpected for the anion adsorption reaction to be slower than the hydrogen desorption reaction, or if both reactions are occurring simultaneously, for the intimate presence of anions to slow the hydrogen reaction. There appears, therefore, to be substantial but not definitive evidence indicating peak III corresponds to specific adsorption of anions at low coordination sites, i.e., structure sensitive anion adsorption. A definitive demonstration that peak III corresponds to structure sensitive anion (specific) adsorption at the pzc could be obtained by observing peak III on stepped surfaces of variable step periodicity in both adsorbing and non-adsorbing electrolytes. Such studies are in progress in this laboratory.

Conclusions From the Present Study

1. Multiple peaks due to hydrogen adsorption-desorption are observed (by cyclic voltammetry) on a clean, annealed, polycrystalline Pt surface in dilute nonadsorbing electrolytes (e.g. HClO_4 or HF). No lattice distortion or sublattice oxide is required to induce hydrogen adsorption into multiple states.
2. Hydrogen adsorption on highly ordered low index surfaces of structure (111)-(1x1) and (100)-(1x1) can be described by the classical model for single site adsorption on a homogeneous surface with a weak interaction between nearest neighbor pairs. Quantitatively, the initial (zero coverage) adsorption free energies were 3.0 kcal/equiv on (111) sites, 6.44 kcal/equiv on (100) sites, and the interaction energy was 4.2×10^{-14} ergs/H-pair (0.6 kcal/mole H-pair).
3. Hydrogen is adsorbed on a highly ordered stepped surface of structure [3(111)-(100)] in multiple bonding states that indicate distinctly different bond energies for adsorption at the (100) step than the (111) terrace. The ratio of charge associated with terrace sites to those at the step was less than the 2:1 geometric

ratio. Hydrogen is bonded at the (100) step in multiple states, one state having an adsorption free energy (9.2 kcal/equiv) higher than that for the (100) single crystal surface. These highest binding energy states are probably characteristic of absorption at surface atoms of low (≤ 7) coordination number.

Comparison with Ref. [33]

The results in the present work are qualitatively similar to the results given in [33] (subsequently referred to as HIK) but quantitative comparison is difficult because different electrolytes were used (1M H_2SO_4 and HClO_4 vs. 1M HF and 0.1M HClO_4 here). HIK found that hydrogen is more strongly bound to ordered (100) surfaces than ordered (111) surfaces, and assigned the two principal peaks in the voltammogram of a polycrystalline surface to hydrogen adsorbed at sites with (100) and (111) local symmetry as we have done here. HIK used a model for hydrogen adsorption that accounted for repulsive nearest neighbor interaction between adsorbed hydrogens and included an interaction term for the effect of $\text{SO}_4^{=}$ and ClO_4^- adsorption, both interactions effectively lowering the bond energy of hydrogen. In this study anion adsorption was assumed to be negligible in HF or 0.1 M HClO_4 , but some preliminary results are presented to suggest that anion adsorption may be structure sensitive and as such would greatly complicate the interpretations of voltammograms in adsorbing electrolytes. The strength of the hydrogen bond is reflected in the HIK analysis by the equilibrium constant K_H , which is equivalent to $\exp(-\Delta G_1^0/RT) \cdot \exp(E_0 F/RT)$, where E_0 is the potential of the NHE relative to the 1M NaCl calomel electrode used by HIK. The values of K_H for (111) and (100) given by HIK were 9×10^{-3} and 0.75, which correspond to ΔG_1^0 values of 1.84 and 6.26 kcal/mole H, respectively, versus 3.0 and 6.44 kcal/mole H in the present work (conversely, the ΔG_1^0 values given here correspond to K_H values of 2.67×10^{-3} and 0.83). The small differences in free energies of adsorption are probably due to the manner in which the anion effect is accounted for. The repulsive interaction parameter used by HIK (B_H in Ref. [33]) is called r here (equals zV/RT) and for the (111) surface the value of r was 6.0, while HIK found 5.7, in close agreement. HIK present an involved discussion as to the nature of the minor (II, III, V) peaks that is not

based on any experiments specifically designed to isolate these effects as done in this work with ordered steps. However, they "postulate that these small peaks are due to chemisorption of hydrogen atoms in the unique surface sites created by self-adsorbed single Pt atoms on the (100) and (111) surfaces," a postulate in essential agreement with the conclusion made here based on results obtained with ordered steps. HIK derived their postulate on the premise that hydrogen bond energy increases with increasing coordinative unsaturation of surface atoms. The present work used an ordered stepped surface to show the first evidence seen (for hydrogen electrosorption) that this premise may indeed be correct. Further investigations using stepped surfaces of variable terrace length and geometry should provide the final answer to the issue of the minor peaks.

There is one point of major disagreement between the two studies, and that is the effect of potential cycling. HIK claim no structural rearrangement of the surface was evident from the LEED patterns after ten or more cycles (2-10 mV/s) between 0 and 1.5V (NHE). This result is in direct contradiction to the results of Fig. 10. However, the LEED pattern shown by HIK (their Fig. 2b) for the (100) surface after 10 cycles has very large, poorly contrasted (01) spots suggesting considerable disorder, as seen in the present work. The place exchange mechanism for the formation of irreversible oxide at potentials above $\approx 1V$ (NHE) suggested by Conway and co-workers [6] would seem to preclude the stability of any surface, regardless of degree of order, from reconstruction when the potential is repeatedly cycled through this oxide region. Clearly, the effects of oxide formation-reduction on the surface structure is an essential and unresolved question requiring much further study.

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References

1. Kunz, H. R. and G. Gruver, J. Electrochem. Soc., 122, 1275 (1975).
2. Romanowski, W., Surf. Sci., 18, 373 (1969).
3. van Hardeveld, R. and F. Hartog, Surf. Sci., 15, 189 (1969).
4. Burton, J. J., Cat. Rev. - Sci. Eng., 9, 209 (1974).
5. Will, F., J. Electrochem. Soc., 112, 451 (1965).
6. Conway, B., H. Angerstein-Kozłowska and W. Sharp, Symp. on Characterization of Adsorbed Species, Ottawa, CIC, June 1974; and H. Angerstein-Kozłowska, W. B. A. Sharp and B. E. Conway, in Proceedings of the Symposium on Electrocatalysis, M. W. Breiter ed., The Electrochemical Society, 1974, pp. 94-114.
7. Kinoshita, K., J. Lundquist, and P. Stonehart, J. Electroanal. Chem., 48, 157 (1973).
8. Ross, P. N., J. Electroanal. Chem., 76, 139 (1977); Extended Abstracts of the Spring Meeting of the Electrochemical Society (Philadelphia), Vol. 77-1, The Electrochemical Society Inc., 1977, abstract #343; in Proceedings of the Symposium on Electrode Materials and Processes for Energy Conversion and Storage, J. D. E. McIntyre, S. Srinivasan, and F. G. Will, eds., The Electrochemical Society, Inc., 1977, pp. 290-307.
9. Huang, J. C., Ph.D. Thesis, Case Western Research University, 1974, and J. C. Huang, W. O'Grady and E. Yeager, J. Electrochem. Soc., 121, 1932 (1977).
10. Palmberg, P. W., in Electron Spectroscopy, ed. D. A. Shirley, North-Holland Amsterdam (1974), p. 835.
11. Palmberg, P. W., G. E. Reach, R. E. Weber and N. C. MacDonald (eds.): Handbook of Auger Electron Spectroscopy, Physical Electronics Ind., Edina, MN, 1972.
12. Somorjai, G., R. Joyner and B. Lang, Proc. Roy. Soc. Lond., A331 (1973) 335.
13. Grant, J. and T. Hass, Surf. Sci., 18, 457 (1969).
14. Photographic methods in LEED analysis are presented by H. B. Lyon, Ph.D. Thesis, University of California at Berkeley, June 1967. The effect of disorder on diffraction patterns is presented in detail by A. Guinier in "X-Ray Diffraction," W. H. Freeman, Chapter 6, from which the discussion here has been fashioned.

Figure Captions

- Figure 1 Schematic of (a) the directly coupled electrochemical-LEED/AES system and (b) the solid PTFE single crystal holder.
- Figure 2 Auger electron spectra for the (100) crystal (a) cleaned and annealed; (b) exposed to 1 atm. argon in the transfer chamber; (c) exposed to the glove box atmosphere; (d) exposed to oxygen free electrolyte and (e) after ion etching. All peaks are from Pt Auger transitions except those indicated.
- Figure 3 Voltammogram for a polycrystalline wire electrode subjected to a pre-treatment of several thousand cycles 0-1.5V at 100 mV/s.
- Figure 4 Idealized structure for the stepped surface formed from a single crystal of nominal orientation (211).
- Figure 5 (a) Calculated LEED pattern for a (S) [3(111)-(100)] structure and the (b) observed LEED pattern at 145V. Open circles in (b) represent observed spots obscured by the sample holder. Notation for the calculated pattern is given in the text.
- Figure 6 Voltammogram for the polycrystalline foil electrode after transfer from the UHV system and after 10 pre-treatment cycles. 100 mV/s.
- Figure 7 (a) Anodic voltammetric sweep for the (111) surface and (b) the isotherm for the (111) surface.
- Figure 8 (a) Anodic voltammetric sweep for the (100) surface and (b) the isotherm for the (100) surface.
- Figure 9 Anodic voltammetric sweep for the (S) [3(111)-(100)] surface (—), superimposed sweeps for (111) and (100) surfaces (---), and their sum (●).
- Figure 10 Angular width of (01) spot in the LEED pattern for a (111) crystal after 10 cycles at 100 mV/s to increasing anodic limits (from 0V).
- Figure 11 Effect of potential cycling on the initially well-ordered (a) (111) and (b) (100) surfaces.
- Figure 12 Idealized structure of the (S) [3(111)-(100)] surface showing the geometry of B_0 and B_5 sites.

Figure Captions (Cont'd)

Figure 13 Theoretical isotherms (---) for a model of lateral interaction between pairs of adsorbed H atoms on the (a) (111) and (b) (100) surfaces and the agreement with the measured coverages (●).

Figure 14 Voltammogram of the well-ordered (111) surface in 1N HF and the change produced by introduction of SO_4^- anions. The shaded area indicates anomalous charge due to specific adsorption of anions at the pzc.

Figure 15 Schematic of a general stepped surface in the notation of Ellis and Schwoebel [32]. The $\vec{a}_i$ specify the terrace structure, $\vec{g}_i$ the step structure.

Appendix

The low energy electron diffraction pattern for a surface structure with a step array can be calculated in the kinematic approximation using the analysis of Ellis and Schwoebel [32]. The geometric intensity distribution was calculated in terms of θ and ϕ which are in turn related to the x, y and z-axis as illustrated in Fig. 15. Terraces are parallel to the xy-plane and steps are parallel to the x-axis. For simplicity of analysis, the incident beam is assumed to be normal to the terrace, or

$$\vec{k} = -\frac{2\pi}{\lambda} \vec{z}$$

Then $\vec{K}$, the difference between the scattered and incident wave vector, is given by

$$\vec{K} = \vec{k}' - \vec{k} = \frac{2\pi}{\lambda} [\cos \theta \vec{x} + \sin \theta \sin \phi \vec{y} + (1 + \sin \theta \cos \phi) \vec{z}] \quad (A1)$$

The intensity distribution is then given by

$$\begin{aligned} I(\theta, \phi) = & \text{const.} \cos^2 [\vec{K} \cdot \frac{1}{2}(\vec{a}_2 + \vec{a}_3)] \cos^2 [\vec{K} \cdot \frac{1}{2}(N\vec{a}_1 + \vec{g}_1 + \vec{g}_2 + \vec{g}_3)] \\ & \times \frac{\sin^2 [\vec{K} \cdot \frac{1}{2}\vec{a}_1(N+1)]}{\sin^2 [\vec{K} \cdot \frac{1}{2}\vec{a}_1]} \times \frac{\sin^2 [\vec{K} \cdot \frac{1}{2}(N\vec{a}_1 + \vec{g}_1 + \vec{g}_2)(n+1)]}{\sin^2 [\vec{K} \cdot (N\vec{a}_1 + \vec{g}_1 + \vec{g}_2)]} \\ & \times \delta(\vec{K} \cdot \vec{a}_2 - m\pi) \end{aligned} \quad (A2)$$

where $(N+1)$ is the number of scattering centers on a terrace and $(n+1)$ is the number of terraces assumed to contribute to the diffraction pattern. The function $\delta(\vec{K} \cdot \vec{a}_2 - m\pi)$ restricts the calculation to just the Bragg angles in the ϕ direction so that I was calculated along a vertical row of diffraction spots. The results of the calculations were plotted in the same format presented by the fluorescent screen of the LEED apparatus using a projection net (u, v) where the lines of constant θ or ϕ were given by $u = R \cos \theta$ and $v = R \sin \theta \sin \phi$. Using a bulk fcc structure with lattice constant $3.92 \text{ \AA}$, the (211) surface (Fig. 4) in the notation of Fig. 15 is: $a_1 = 4.80$, $a_2 = 1.385$, $a_3 = 2.40$, $g_1 = 1.60$, $g_2 = 2.26$, $g_3 = 0$, all in $\text{\AA}$, and $N = 1$. The calculated diffraction pattern is shown in Fig. 5(a) for 143V using $n = 8$, corresponding to an electron scattering coherence length of $\approx 70 \text{ \AA}$, the upper limit of coherence realized in a LEED apparatus of the type used in this work. The relative intensity of the beam is reflected in the type and size of spot drawn: $\bullet$ -1; $\bigcirc$ -0.5; $\bigcirc$ -0.25; $\bigcirc$ -0.125; $\circ$ -0.0625; $\cdot$ -0.03.

In contrast to the Pt(S) [6(111)-(100)] surface studied by Lang et. al. [18], the split spots for the [3(111)-(100)] surface are much lower in intensity, being an order of magnitude less intense than an unsplit spot, e.g. the (01) split spots vs. the unsplit(10) spot of Figure 5(a). This is due to the reduced number of scattering centers along a terrace on this surface. There was excellent agreement in the distance between split spots between the computed and experimental patterns, and even reasonable agreement in relative intensities of split spots. Similar results were obtained at other voltages.

(a)

28

(b)

Pt(S) $[3(111)-(100)]$

(a)

(b)

(a)

(b)

Pt(s) [3(111)-(100)]

(a)

(b)

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